



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C07F 7/08, C07C 57/42 A61K 7/44	A1	(11) International Publication Number: WO 92/20690 (43) International Publication Date: 26 November 1992 (26.11.92)
(21) International Application Number: PCT/EP92/01001 (22) International Filing Date: 7 May 1992 (07.05.92) (30) Priority data: 9110123.8 10 May 1991 (10.05.91) GB (71) Applicant (for all designated States except US): GIVAUDAN-ROURE (INTERNATIONAL) S.A. [CH/CH]; CH-1214 Vernier (CH). (72) Inventors; and (75) Inventors/Applicants (for US only): FRATER, Georg [CH/CH]; 5 Turikumstrasse, CH-8610 Uster (CH). SCHWARZENBACH, Rolf [CH/CH]; 1 Köhlbergstrasse, CH-8405 Winterthur (CH). VAN OYCKE, Stephane, François, Marie [BE/GB]; 53 Glamorgan Street, Barry, South Glamorgan CF6 8JP (GB).	(74) Agent: URECH, Peter; P.O. Box 3255, CH-4002 Basle (CH). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent), US. Published With international search report. With amended claims.	
(54) Title: ORGANOSILOXANES FOR USE AS SUNSCREEN AGENTS		
$\text{O}_{\frac{3-a}{2}} \text{Si}(\text{R})_a - \text{C}(\text{R}^1) = \text{CH} - (\text{CR}^1)_2^n - \text{O} - \text{C}_6\text{R}^2\text{H}_2 - \text{CH} = \text{C} - [\text{C}(\text{O})\text{OR}^3]_2 \quad (\text{i})$ $\text{R}''\text{SiO}_{\frac{4-b}{2}} \quad (\text{ii})$ $- \text{C}(\text{R}^1) = \text{CH} - (\text{CR}^1)_2^n - \text{O} - \quad (1)$		
(57) Abstract <p>Novel organosiloxane compounds have at least one unit (i), any other units being present in this organosiloxane are (ii), wherein R is a C₁₋₈ alkyl or aryl, R¹ is H or a C₁₋₅ alkyl, R² is H, C₁₋₅ alkyl or OR¹, R³ is a C₁₋₅ alkyl, R'' is H, a monovalent C₁₋₈ hydrocarbon or halogenated hydrocarbon group, a is 0, 1 or 2, b 0, 1, 2 or 3 and n 1 to 6, provided the group (1) and the two R² groups are linked to the aromatic ring at the para- and meta-positions in relation to the group -CH=C[C(O)OR³]₂. The compounds are useful as UV sunscreens. Compositions containing them are also included.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

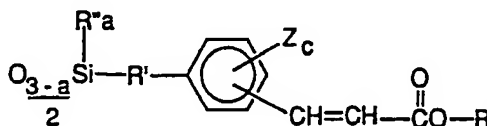
AT	Austria	FI	Finland	MI	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

ORGANOSILOXANES FOR USE AS SUNSCREEN AGENTS

This invention is concerned with novel organosilicon compounds which are effective in absorbing ultra violet radiation and is also
 5 concerned with a process of preparing such compounds.

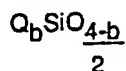
A number of organic compounds, generally organic acids and derivatives thereof, are known to be chromophores having U.V.-absorbing properties and are employed on a commercial scale as ingredients in sunscreen preparations or as plastic additives. Although
 10 such materials function adequately they are easily removed from the substrate to which they have been applied. For example, cosmetic sunscreen preparations can be removed during bathing thus requiring repeated applications if protection is to be maintained. It is also desirable that the active ingredient remain on the surface of the skin
 15 rather than penetrate into or through the skin.

Compounds which overcome this problem to a certain extent are disclosed for example in European Patent Specification 305 059, which provides organosilicon compounds having at least one unit of the general formula



- 2 -

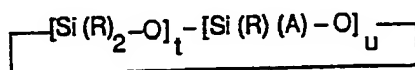
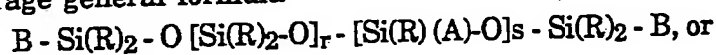
any other units present in the said siloxanes being those represented by the general formula



wherein R represents a C₁₋₁₈ alkyl group, R' is a divalent alkylene or oxyalkylene group having from 2 to about 20 carbon atoms, or a divalent alkenylene or oxyalkenylene group having from 2 to 20 carbon atoms, wherein the carbon-carbon double bond is adjacent to the silicon atom, R" is a halogen atom, an alkyl, aryl, alkoxy or alkoxyalkoxy group having less than 9 carbon atoms, Q represents a hydrogen atom, a monovalent C₁₋₁₈ hydrocarbon or halogenated hydrocarbon group, Z is an alkyl or an alkoxy group having from 1 to 8 carbon atoms or a hydroxyl group, a and b each have a value of 0, 1, 2 or 3 and c is 0 or 1, provided that at least one of Z and R' is linked to the multivalent aryl group via an ether linkage.

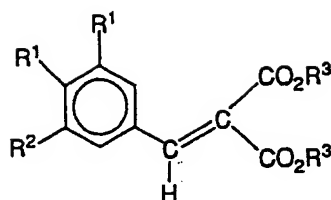
It was found, however, that although the materials described above were, in comparison with the prior art, less susceptible to hydrolysis at the ester linkage, for example by enzymatic hydrolysis on the skin when these materials were used as cosmetic sunscreen agents, they were not sufficiently photostable when exposed to UV irradiation.

EP publication 392 882 discloses the use of diorganopolysiloxanes with a benzalmalonate functionality in cosmetic applications. The diorgano-polysiloxanes which are useful in said application have the average general formula



wherein R is C₁₋₁₀ alkyl, phenyl or trifluoropropyl, B is R or A, r is from 0 to 200, s is from 0 to 50, u is from 1 to 20, t is from 0 to 20, t+u is at least 3, there being at least one group A per molecule and A denotes a structure of the general formula

- 3 -

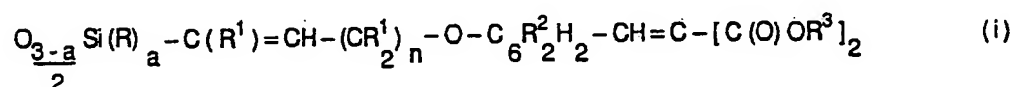


wherein R¹ is H, OH, trimethylsiloxy, C₁₋₆ alkoxy or a divalent group -(O)_n-(CH₂)_p-CH(R'')-CH₂-, n is 0 or 1, p is 1 to 10, R'' is H or
 5 C₁₋₄ alkyl, R² is H, C₁₋₆ alkyl or C₁₋₆ alkoxy, R³ is C₁₋₈ alkyl, at least one of the R¹ groups being the divalent group.

We have found that although the materials described in both above identified references perform well in many applications, and although there is a reduction in the amount of chromophore which penetrates
 10 through the skin when applied thereto in comparison with the amount of chromophore which penetrates when it has been applied as a pure compound (i.e. not linked to an organosilicon compound), there is still a need to further reduce the amount of penetration through the skin.

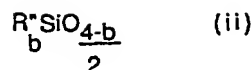
We have now found that if certain novel chromophores are used in
 15 the preparation of organosilicon compounds, improved cosmetic preparations, effective in absorbing ultra violet radiation can be obtained.

According to a first aspect of the invention there is provided an organosiloxane compound having at least one unit of the general
 20 formula

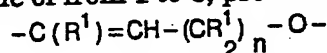


25 any other units present in the said siloxanes being those represented by the general formula

- 4 -



wherein R represents a C₁₋₈ alkyl or an aryl group, R¹ is a hydrogen atom or a C₁₋₅ alkyl group, R² is a hydrogen atom, a C₁₋₅ alkyl group or a group OR¹, R³ is a C₁₋₅ alkyl group, R" represents a hydrogen atom, a monovalent C₁₋₈ hydrocarbon or halogenated hydrocarbon group, a has a value of 0, 1 or 2, b has a value of 0, 1, 2 or 3 and n has a value of from 1 to 6, provided that the

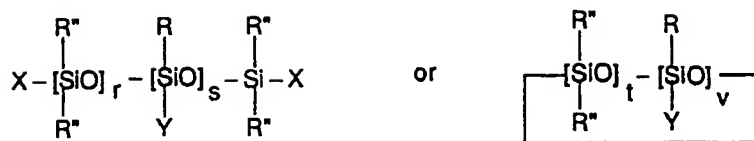


group and the two R² groups are linked to the aromatic ring at the para and both meta positions in relation to the group

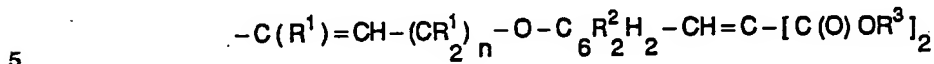


In the general formula of the organosilicon compounds of the invention R may be for example methyl, ethyl, butyl or phenyl. R" is hydrogen or a monovalent hydrocarbon or halogenated hydrocarbon group having less than 8 carbon atoms, for example alkyl, alkenyl, aryl, alkaryl, aralkyl and halogen substituted alkyl, alkenyl, aryl, alkaryl and aralkyl groups. Examples include methyl, ethyl, vinyl, phenyl and 3,3,3- trifluoropropyl. R³ denotes alkyl groups having up to 5 carbon atoms for example methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, isobutyl, pentyl and neopentyl. R¹ is either a group R³ or a hydrogen atom and R² is a group R¹ or a group OR¹. It is preferred that at least 80% of all R and R" groups are methyl groups, most preferably substantially all R and R" groups are methyl groups. It is also preferred that R¹ is either hydrogen, methyl or ethyl, most preferably hydrogen. Preferably each R² group is H or one R² group is a hydrogen, while the other one is an alkoxy group, preferably methoxy or ethoxy. R³ is preferably methyl or ethyl. a is preferably 1 while b is preferably 2, making the organosilicon compound a substantially linear or cyclic diorgano-siloxane polymer. However, if the diorganosiloxane is a substantially linear polymer at least two endblocking units must be present, thus requiring the presence of 2 units in which a has a value of 2, two units in which the value of b is 3 or one unit wherein a is 2 and one unit in which b is 3. n is preferably 1, 2 or 3. Suitable preferred polymers have therefore either the general formula

- 5 -

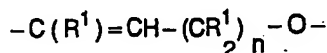


wherein R and R'' are as defined above, X denotes a group Y or a group R'' and Y denotes a group of the formula

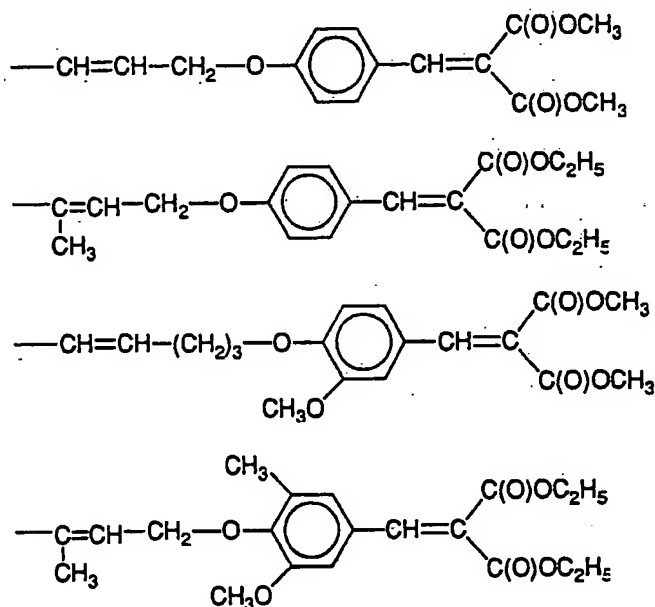


r has a value of from 0 to 100, s has a value of from 0 to 20, whereby at least one X denotes Y in the case that s=0, t has a value of from 0 to 10, v has a value of from 1 to 10 and v+t has a value of at least 3.

In the substituent Y of the organosilicon compounds according to the invention, the group



may occupy the meta-position or the para-position of the aromatic ring in relation to the group $-\text{CH}=\text{C}[\text{C}(\text{O})\text{OR}^3]_2$. Preferably the para-position is thus occupied. The groups R² occupy the remaining two positions out of the para- and meta-positions in relation to the group $-\text{CH}=\text{C}[\text{C}(\text{O})\text{OR}^3]_2$. Examples of preferred substituents Y thus include



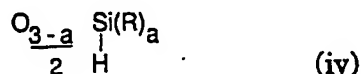
The organosilicon compounds of the present invention have at least one unit falling within the general formula (i), preferably at least 2.

Suitable organosilicon compounds are polymeric materials which may be homopolymers consisting only of such units (i), or they may be copolymers containing both units (i) and units having the general formula (ii). The organosilicon compounds may vary from freely flowing liquids to highly viscous gum-like materials or resinous solids. Preferred, at least for cosmetic applications, are the liquid substantially linear organosiloxane homopolymers and copolymers, for example those having a viscosity of from 100 to 20000 m²/s, more preferably 500 to 5000 mm²/s as these are more easily mixed with other ingredients to make cosmetic compositions and as they will spread more easily onto the skin.

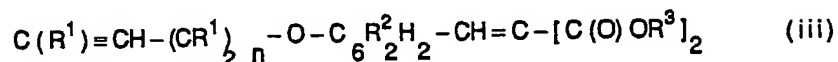
Organosilicon compounds of the invention which are especially preferred are those wherein the number of units (i) is limited to a maximum of 20% of the total number of siloxane units in the molecule. For maximum efficiency in its U.V. absorbing property it is preferred that the number of units (i) be limited to 10% or less of the total. The units of formula (i) may be distributed randomly in an organosiloxane polymer, they may be end-blocking units of the polymer or they may be located at the end of the polymer and pending in chain of the polymer at the same time. Units of the general formula (i) are preferably situated at the end of the organosiloxane polymer forming one or more endblocking units of the polymer. In the most preferred organosilicon compounds which are substantially linear polyorganosiloxane polymers, both endblocking units have a structure represented by the general formula (i), while all other units are according to the general formula (ii). The most preferred organosilicon compounds have two units of the formula (i) and a larger number of units according to the general formula (ii), e.g. 8 to 90, especially 8 to 40.

The organosilicon compounds according to the invention are effective in absorbing ultra violet radiation in the erythemic region (290 - 320nm) which makes them particularly suitable for use in cosmetic sunscreen preparations where absorption in the UV-B region is particularly desirable. Most preferred for this application are those that have a maximum absorbance at 300 - 320nm.

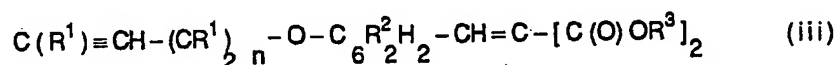
The organosilicon compounds of the present invention can, quite generally, be prepared by the reaction of an organosilicon compound in which each unit (i) is replaced with a unit having the general formula



5 with a chromophore of the general formula



10 These chromophores are in themselves novel compounds and the invention therefore includes in one of its aspects a compound of the formula

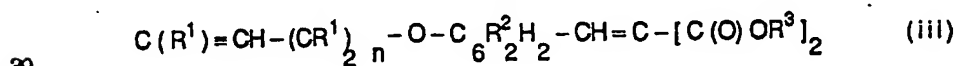


15 wherein R¹ is a hydrogen atom or a C₁₋₅ alkyl group, R² is a hydrogen atom, a C₁₋₅ alkyl group or a group OR¹, R³ is a C₁₋₅ alkyl group and n has a value of from 1 to 6, provided that the group containing the unsaturated carbon-carbon triple bond and the two R² groups are linked to the two meta-positions and to the para-position of the aromatic ring in relation to the ester containing group.

20 Compounds of the general formula (iii) may be prepared e.g. by reacting a hydroxy or dihydroxy benzaldehyde with halogenopropyne, followed by a further reaction with a diester of malonic acid. The first reaction is preferably carried out in the presence of a suitable solvent, e.g. acetone, preferably at reflux temperatures. The presence of a catalyst is also preferred. The second reaction is also preferably carried out in the presence of a solvent, e.g. toluene at reflux temperatures. The
25 final product of formula (iii) is a light brown crystal.

The invention also includes a process for the preparation of organosilicon compounds of the kind specified herein, which comprises reacting together

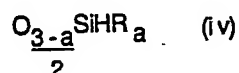
(A) a compound of the general formula



30

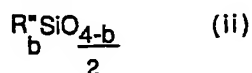
- 8 -

wherein R¹ is a hydrogen atom or a C₁₋₅ alkyl group, R² is a hydrogen atom, a C₁₋₅ alkyl group or a group OR¹, R³ is a C₁₋₅ alkyl group and n has a value of from 1 to 6, provided that the group containing the unsaturated triple bond and the two R² groups are linked to the two meta-positions and to the para-position of the aromatic ring in relation to the group
 5 -CH=C-[C(O)OR³]₂ and
 (B) an organosilicon compound having at least one unit of the general formula



10

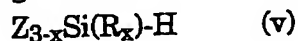
any other units present in the organosilicon compound being those represented by the general formula



wherein R, R'', a and b are as hereinabove defined.

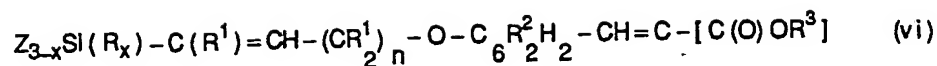
15 The reaction is preferably carried out employing stoichiometric proportions of (A) and (B) or a slight stoichiometric excess of (A). However, a stoichiometric deficiency of (A) can be employed if residual silicon-bonded hydrogen is desired in the product.

Alternatively polymeric organosilicon compounds of the invention
 20 can also be obtained by first preparing the corresponding hydrolysable silane, employing in place of the organosilicon compound (B) the corresponding SiH containing silane (C) which has the general formula



25 wherein R is as defined above, Z is a hydrolysable group, preferably alkoxy having 1 to 8 carbon atoms and x has a value of 0, 1 or 2.

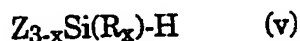
The silane (D) resulting from this reaction may be submitted thereafter to cohydrolysis with a further hydrolysable silane or equilibration with (E) cyclic or (F) linear polyorganosiloxanes consisting essentially of units of the formula (ii). Silanes (D) which can be used in
 30 this method are novel in themselves and are included in the scope of the present invention. Silanes (D) have the general formula



wherein R, R¹, R², R³, Z, x and n are as defined above.

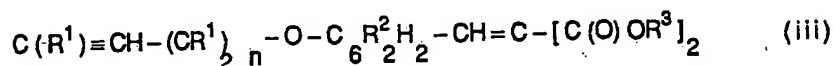
Thus, in more detail, the process comprises

- 5 I) the preparation of a hydrolysable silane by reacting a silane of the general formula



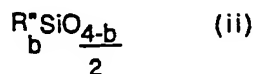
wherein R represents a C₁₋₈ alkyl or aryl group, Z is a hydrolysable group and x has a value of 0, 1 or 2,

- 10 with a compound of the general formula



- 15 wherein R¹ is a hydrogen atom or a C₁₋₅ alkyl group, R² is a hydrogen atom, a C₁₋₅ alkyl group or a group OR¹, R³ is a C₁₋₅ alkyl group and n has a value of from 1 to 6, provided that the group containing the unsaturated triple bond and the two R² groups are linked to the two meta-positions and to the para-position of the aromatic ring in relation to the group -CH=C-[C(O)OR³]₂, and

- 20 II) submitting the hydrolysable silane to cohydrolysis or equilibration with cyclic or linear polydiorganosiloxanes consisting essentially of units of the formula



wherein R'' represents a hydrogen atom a monovalent C₁₋₈ hydrocarbon or halogenated hydrocarbon, and b has a value of 0, 1, 2 or 3.

- 25 Z is preferably an alkoxy group having from 1 to 8 carbon atoms.

As concerns the cohydrolysis, such reaction will conveniently be in conjunction with other hydrolysable silanes (e.g. diorgano-dihalosilanes, or diorgano-alkoxysilanol, etc.) or with siloxanes

- 10 -

having hydrolysable endgroups (e.g. α,ω dihydroxy polydimethylsiloxanes).

5 As concerns the equilibrium aspect on the linear or cyclic polydiorganosiloxanes, cyclic siloxanes will conveniently have the general formula $[R^2SiO]_n$, wherein n has a value of from 3 to 9, and linear polydiorganosiloxanes are usually used as end-blocking units, and will be short chain triorganosiloxane end-blocked polydiorgano-siloxanes (in the shortest form hexa-organodisiloxane $[R_3Si-O-SiR_3]$).

10 This alternative process involves thus technique which is known per se.

In order to obtain the particularly preferred polymeric organosilicon compounds of the invention the reaction is carried out in
15 such a way that in the reaction product at least one siloxane unit and no more than 20% of the total number of siloxane units has a structure according to formula (i). This may be achieved by reacting polymeric organosilicon compounds (B) which have a maximum of 20 mole % silicon-bonded hydrogen atoms, with stoichiometric amounts of
20 compound (A). Excess amounts of (A) may also be used in this case. If residual SiH groups are desired in the organosilicon compound product less than stoichiometric amounts of compound (A) may be employed. The particularly preferred polymeric organosilicon compounds of the invention may also be obtained by reacting polymeric organosilicon
25 compounds (B) having more than 20 mole % silicon-bonded hydrogen atoms, with less than stoichiometric amounts of compound (A). Most preferably, however, organosilicon compounds (B) are employed which are polydiorganosiloxanes endblocked with diorganohydrosiloxane units provided the siloxane has a minimum chain length of 10 silicon
30 atoms.

The reaction between (A) and (B) may be carried out employing known procedures for the addition of silicon-bonded hydrogen atoms to groups containing aliphatic unsaturation. Thus, such reactions are generally catalysed by a platinum group metal or a compound or
35 complex of such a metal. Examples of catalysts which may be employed

in the reaction between (A) and (B) are platinum on carbon, chloroplatinic acid, platinum acetyl acetonate, complexes of platinum compounds with unsaturated compounds e.g. olefins and vinyl siloxanes, complexes of rhodium and palladium compounds and
5 complexes of platinum compounds supported on inorganic substrates. The addition reaction may be performed at reduced, atmospheric or increased pressure. It is generally preferred to employ a solvent e.g. toluene or xylene in the reaction mixture although the presence of a solvent is not essential. It is also preferred to carry the reaction out at
10 elevated reaction temperatures e.g. from about 50° C up to the reflux temperature of the reaction mixture.

The organosilicon compounds of this invention have similar UV absorbance characteristics to those disclosed in the prior art. They are useful as agents for preventing sunburn and are thus useful in skin
15 care and hair care applications. They may be applied per se to the skin or hair but are more preferably formulated into cosmetic compositions with, for example, inert carriers e.g. solvents such as water, ethanol, isopropanol, glycerine and mineral oil and cream base materials such as stearic acid, propylene glycol, beeswax and cetyl alcohol. Other
20 conventional ingredients e.g. perfumes and known U.V. absorbing substances may also be included in the formulated compositions. The organosilicon compounds of the present invention are also useful in the coating of substrates e.g. wood, plastics or metal, to which they may be applied either per se or as additives to coating compositions or they may
25 be incorporated as additives in plastics materials.

The following examples, in which parts and percentages are expressed by weight illustrate the invention.

Example 1

Preparation of propanedioic
30 { [4- (2-propynyloxy)phenyl]methylene} -diethyl ester (the most preferred compound).

To a stirred suspension of 4-hydroxybenzaldehyde (425.8g) and K₂CO₃ (807.6g) in acetone (2,960ml) at reflux temperature of about 60° C under a nitrogen atmosphere, was added dropwise 3-bromo-propyne
35 (502.4g) over a period of 2 hours. The reaction was heated at reflux for 3

- 12 -

more hours. After cooling to room temperature the reaction mixture was filtered and the excess of K_2CO_3 removed and washed several times with acetone. The filtrate was washed with saturated aqueous solution of $NaHCO_3$ and $NaCl$. The aqueous phase was extracted with diethyl
5 ether. The combined organic extracts were dried over Na_2SO_4 , filtered and concentrated to a volume of 1 litre. The solution was kept in the refrigerator overnight. The crystals were filtered out and washed with cold diethyl ether. The filtrate was kept in the refrigerator and some more crystals were formed and removed. This procedure was repeated 3
10 times resulting in 1,385.26g of 4-(2-propynyloxy) benzaldehyde in 83% yield. The material was analysed by gas chromatography, and shown to be 99.9% pure. Infrared and mass spectroscopic analysis confirmed the structure.

The resulting compound (449.2g) was added in small amounts to a
15 stirred solution of diethyl malonate (448.5g), piperidine (23.84g), toluene (1,400ml) and acetic acid (59g) at about 50° C. The acetic acid had been added in three equal portions after 1, 1.5 and 2 hours respectively. The reaction mixture was heated to reflux. After four hours the mixture was allowed to cool to room temperature and washed with saturated
20 aqueous solution of $NaHCO_3$ and $NaCl$, dried with Na_2SO_4 , filtered and concentrated, giving 853.4g of a dark brown oily product. Diethyl ether (458ml) and n-hexane (358ml) were added and the solution kept in a refrigerator overnight. The solution was filtered, giving 564.8g of light brown crystals (67% yield) having a melt-ing point of 45.5 to 48° C.
25 Recrystallisation in ethanol and n-hexane yielded 543g of the title compound as light brown crystals. Analysis revealed a melting point of 48.5 to 49.5° C and a purity by capillary gas chromatography of 99.9%.

Example 2

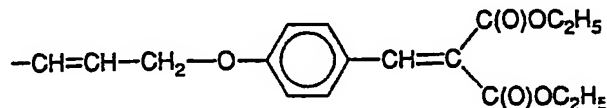
Preparation of propanedioic
30 { [4- (2-propynyloxy)phenyl]methylene} -dimethyl ester

The procedure of the above method was repeated except that dimethyl malonate was used instead of diethyl malonate.

Example 3

- 13 -

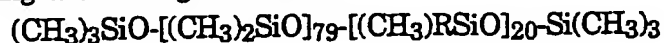
5g of { [4- (2-propynyloxy)phenyl]methylene} -diethyl ester
 were dissolved in 20g of toluene and heated under nitrogen to about 80°
 C. 13.2g of a hydrosiloxane having a degree of polymerisation of 20 and
 10mpc SiH groups (3.62% SiH) were then added dropwise after a
 5 platinum complex was also added, giving 10⁻⁴ mole of Pt per mole of SiH
 of the hydro-siloxane. The mixture was heated to reflux and maintained
 until all SiH had disappeared of the infrared spectroscopic analysis. It
 was then allowed to cool to room temperature. The toluene was then
 evaporated to leave after washing 16.5g of a slightly brown polymer
 10 having the average structure
 R-[(CH₃)₂SiO]₂₀-R, wherein R has the formula



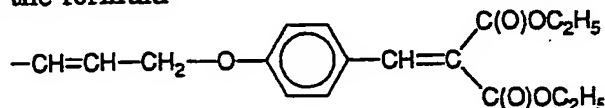
Only 1.6% by weight of the total reaction product of unreacted { [4- (2-
 propynyloxy)phenyl]methylene} -diethyl ester was present in the
 15 endproduct.

Example 4

10g of { [4- (2-propynyloxy)phenyl]methylene} -diethyl ester
 20 were dissolved in 10g of toluene and heated under nitrogen to about 80°
 C. 13.2g of a hydrosiloxane having a degree of polymerisation of 100
 and 20mpc SiH groups (8.43% SiH) were then added dropwise after a
 platinum complex was also added, giving 10⁻⁴ mole of Pt per mole of SiH
 of the hydro-siloxane. The mixture was heated to reflux and maintained
 25 until all SiH had disappeared of the infrared spectroscopic analysis. It
 was then allowed to cool to room temperature. The toluene was then
 evaporated to leave after washing 21.2g of a hazy, very viscous polymer
 having the average structure



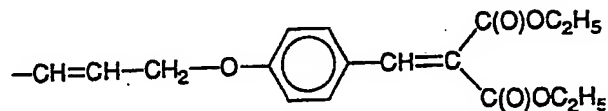
30 wherein R has the formula



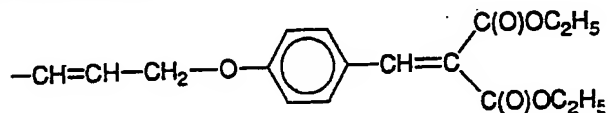
Examples 5 and 6

Similar procedures as described for Examples 3 and 4 were used to make polymers with the average formulae

- 5 (5) $R-[(CH_3)_2SiO]_2-R$ wherein R has the formula



- (6) $(CH_3)_3SiO-[(CH_3)_2SiO]_6-[(CH_3)RSiO]_2-Si(CH_3)_3$
wherein R has the formula

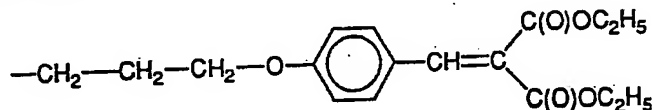


10

Comparative Example 1

A similar procedure as described for Examples 3 and 4 was used to make a polymer with the average formula

- 15 $Q-[(CH_3)_2SiO]_{20}-Q$
wherein Q has the formula

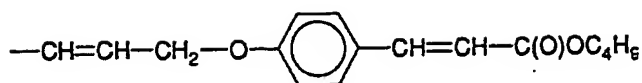


3.3% by weight of the total reaction product of unreacted
{ [4-(2-allyloxy)phenyl]methylene}-diethyl ester was present in the
20 endproduct.

Comparative Example 2

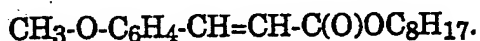
A similar procedure as described for Examples 3 and 4 was used to make a polymer with the average formula

- 25 $(CH_3)_3SiO-Si(CH_3)_2-OSi(CH_3)_3$,
wherein Z has the formula



Comparative Example 3

Commercially available Parsol MCX was used which has the
5 formula



UV Absorption Tests

Comparative Example 1 and Example 1 were both tested for their
10 absorption at 300nm (E 1%,cm). To this effect the samples were
dissolved in tetrahydrofuran. Example 1 showed an absorption of 211
while Comparative Example 1 only gave a value of 83. This shows that
the organosilicon compounds according to the invention are better than
the prior art.

15 Stability and water resistance

Each sample was tested and found satisfactory in view of the
stability to UV radiation and its resistance to washing off with water.

Skin Penetration Tests

Invitro penetration tests were carried out on rat skin. The samples
20 were dissolved in tetrahydrofuran at a concentration of 10%, and this
was applied to the skin at a dosage of 30 µl per 5 cm² and penetration
was checked after 16 hours. After the test the penetration level was
inspected by measuring the amount of material on the skin surface, in
the horny layer, in the upper part of the skin, in the lower part of the
25 skin and in the chamber (vitro). This was tested by wiping the surface to
remove all non-penetrated material and placing it in a glass vial,
followed by stripping the cleaned skin several times with adhesive tape
to remove the horny layer and placing the tapes in a second glass vial.
The stripped skin was then divided in an upper and lower part. The
30 upper part was homogenised in 10ml of tetrahydrofuran and placed in a
third vial, while the lower part was treated separately in the same way
and placed in a fourth vial. The chamber liquid was then placed in a

fifth vial, the chamber rinsed with tetrahydrofuran which was also added to the vial.

The content of each of the vials was then extracted with tetrahydrofuran and analysed by high performance liquid chromatography. The most preferred materials are those where the amount of penetration in the lower skin is minimal. The results, based on an average from 2 experiments each, are shown in Table I.

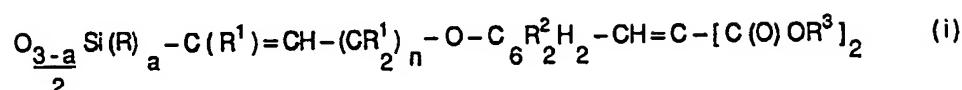
Table I: Skin penetration values in %

	Example	Skin surface	Horny layer	Upper skin	Lower skin	Chamber liquid
10	3	90.7	1.6	7.5	0.2	<0.1
	4	73.7	24.0	2.1	0.2	<0.1
	5	89.4	6.7	3.5	0.4	<0.1
	6	98.5	3.2	0.9	0.4	<0.1
15	Comp. 1	88.9	6.1	3.3	1.7	<0.1
	Comp. 2	52.2	6.8	7.8	3.2	<0.1
	Comp. 3	46.3	3.0	8.5	2.8	9.4

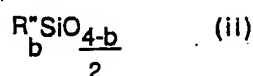
It is clear that materials according to the invention have less penetration through the skin than prior art materials.

Claims

1. An organosiloxane compound having at least one unit of the
5 general formula

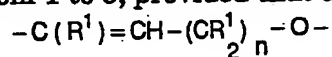


any other units present in the said siloxanes being those represented by the general formula



10

- wherein R represents a C₁₋₈ alkyl or an aryl group, R¹ is a hydrogen atom or a C₁₋₅ alkyl group, R² is a hydrogen atom, a C₁₋₅ alkyl group or a group OR¹, R³ is a C₁₋₅ alkyl group, R'' represents a hydrogen atom, a monovalent C₁₋₈ hydrocarbon or halogenated
15 hydrocarbon group, a has a value of 0, 1 or 2, b has a value of 0, 1, 2 or 3 and n has a value of from 1 to 6, provided that the



group and the two R² groups are linked to the aromatic ring at the para- and both meta-positions in relation to the group -CH=C[C(O)OR³]₂.

20

2. An organosiloxane compound according to Claim 1 wherein at least 80% of all R and R'' groups are methyl groups.
3. An organosiloxane compound according to Claim 1 or 2 wherein
25 each R¹ is selected from hydrogen, methyl and ethyl.

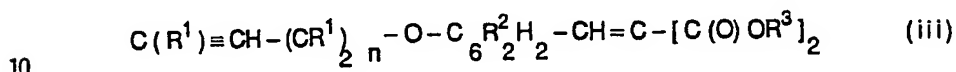
- 18 -

4. An organosiloxane compound according to anyone of the preceding claims wherein at least one R² group is a hydrogen, the other being hydrogen, methoxy or ethoxy.
5. An organosiloxane compound according to anyone of the preceding claims wherein R³ is methyl or ethyl.
6. An organosiloxane compound according to anyone of the preceding claims wherein each R¹ and R² group is hydrogen.
7. An organosiloxane compound according to anyone of the preceding claims which is a substantially linear or cyclic diorganosiloxane polymer.
8. An organosiloxane compound according to anyone of the preceding claims wherein the group
- $$-C(R^1)=CH-(CR_2^1)_n-O-$$
- occupies the para-position on the aromatic ring in relation to the group $-CH=C[C(O)OR^3]_2$, and both groups R² occupy the meta-positions on the aromatic ring in relation to the group $-CH=C[C(O)OR^3]_2$.
9. An organosiloxane compound according to anyone of the preceding claims wherein the number of units (i) is limited to a maximum of 20% of the total number of siloxane units in the molecule.
10. An organosiloxane compound according to anyone of the preceding claims wherein the number of units (i) be limited to 10% or less of the total number of units.

11. An organosiloxane compound according to anyone of the preceding claims wherein units of the general formula (i) are situated at the end of the organosiloxane compound.

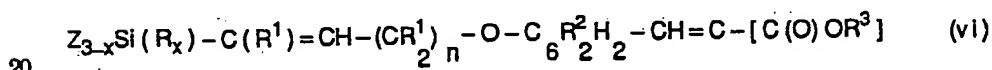
5 12. An organosiloxane compound according to anyone of the preceding claims having two end-blocking units of formula (i) and from 8 to 90 units of the general formula (ii).

13. A compound of the formula



wherein R^1 is a hydrogen atom or a C_{1-5} alkyl group, R^2 is a hydrogen atom, a C_{1-5} alkyl group or a group OR^1 , R^3 is a C_{1-5} alkyl group and n has a value of from 1 to 6, provided that the group containing the unsaturated carbon-carbon triple bond and the two R^2 groups are linked to the two meta-positions and to the para-position on the aromatic ring in relation to the ester containing group.

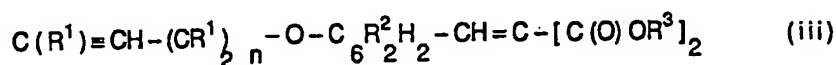
14. A silane having the general formula



wherein R , R^1 , R^2 , R^3 and n are as defined above, Z is a hydrolysable group and x has a value of 0, 1 or 2.

15. A process for the preparation of the organosilicon compounds of claim 1 which comprises reacting together

(A) a compound of the general formula



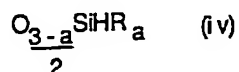
wherein R^1 is a hydrogen atom or a C_{1-5} alkyl group, R^2 is a hydrogen atom, a C_{1-5} alkyl group or a group OR^1 , R^3 is a C_{1-5} alkyl

- 20 -

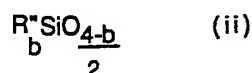
group and n has a value of from 1 to 6, provided that the group containing the unsaturated triple bond and the two R² groups are linked to the two meta-positions and to the para-position of the aromatic ring in relation to the group

5 -CH=C-[C(O)OR³]₂ and

(B) an organosilicon compound having at least one unit of the general formula



any other units present in the organosilicon compounds being those represented by the general formula



wherein R, R'', a and b are as hereinabove defined.

16. A process according to Claim 15, wherein stoichiometric proportions of (A) and (B) or a slight stoichiometric excess of (A) are used.

17. A process for the preparation of the organosilicon compounds of claim 1, which comprises submitting a hydrolysable silane of claim 14 to cohydrolysis with a further hydrolysable silane or submitting it to equilibration with a cyclic or linear polydiorganosiloxane exhibiting the units of formula (ii) as given in Claim 1.

18. A cosmetic or a coating composition comprising an organosiloxane compound according to anyone of Claims 1 to 12.

19. The use of an organosiloxane compound according to anyone of Claims 1 to 12 as absorber for the ultraviolet light.

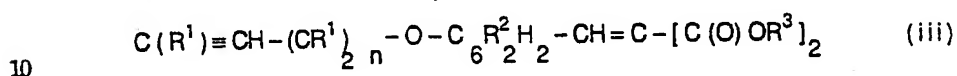
AMENDED CLAIMS

[received by the International Bureau on 2 October 1992 (02.10.92);
original claim 14 amended; remaining claims unchanged (1 page)]

11. An organosiloxane compound according to anyone of the preceding claims wherein units of the general formula (i) are situated at the end of the organosiloxane compound.

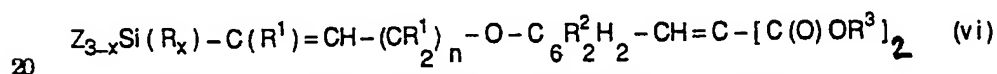
5 12. An organosiloxane compound according to anyone of the preceding claims having two end-blocking units of formula (i) and from 8 to 90 units of the general formula (ii).

13. A compound of the formula



wherein R¹ is a hydrogen atom or a C₁₋₅ alkyl group, R² is a hydrogen atom, a C₁₋₅ alkyl group or a group OR¹, R³ is a C₁₋₅ alkyl group and n has a value of from 1 to 6, provided that the group containing the unsaturated carbon-carbon triple bond and the two R² groups are linked to the two meta-positions and to the para-position on the aromatic ring in relation to the ester containing group.

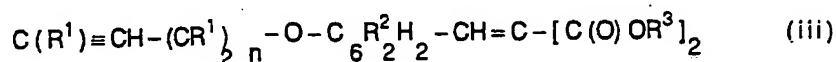
14. A silane having the general formula



wherein R, R¹, R², R³ and n are as defined above, Z is a hydrolysable group and x has a value of 0, 1 or 2.

15. A process for the preparation of the organosilicon compounds of claim 1 which comprises reacting together

(A) a compound of the general formula



wherein R¹ is a hydrogen atom or a C₁₋₅ alkyl group, R² is a hydrogen atom, a C₁₋₅ alkyl group or a group OR¹, R³ is a C₁₋₅ alkyl

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 92/01001

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁴ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 07 F 7/08, C 07 C 57/42, A 61 K 7/44																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <div style="display: flex; justify-content: space-between;"> <div style="width: 30%; border-bottom: 1px solid black;">Classification System</div> <div style="width: 70%; border-bottom: 1px solid black;">Classification Symbols</div> </div> <div style="display: flex; justify-content: space-between; padding: 5px;"> <div style="width: 30%;">IPC⁵</div> <div style="width: 70%;">C 07 F, C 07 C 57/00, A 61 K</div> </div> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched ⁸</div>																	
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category ⁹</th> <th style="width: 60%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A1, 0 358 584 (RHONE POULENC) 14 March 1990 (14.03.90), see claim 1. ---</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A1, 0 392 882 (L'OREAL) 17 October 1990 (17.10.90), see claims 1, 3. ---</td> <td style="text-align: center; vertical-align: top;">1, 18</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A2, 0 305 059 (DOW CORNING) 01 March 1989 (01.03.89), see claim 1. ---</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A2, 0 350 314 (SHISEIDO) 10 January 1990 (10.01.90), see claims 1, 6. -----</td> <td style="text-align: center; vertical-align: top;">1, 18</td> </tr> </tbody> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	EP, A1, 0 358 584 (RHONE POULENC) 14 March 1990 (14.03.90), see claim 1. ---	1	A	EP, A1, 0 392 882 (L'OREAL) 17 October 1990 (17.10.90), see claims 1, 3. ---	1, 18	A	EP, A2, 0 305 059 (DOW CORNING) 01 March 1989 (01.03.89), see claim 1. ---	1	A	EP, A2, 0 350 314 (SHISEIDO) 10 January 1990 (10.01.90), see claims 1, 6. -----	1, 18
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³															
A	EP, A1, 0 358 584 (RHONE POULENC) 14 March 1990 (14.03.90), see claim 1. ---	1															
A	EP, A1, 0 392 882 (L'OREAL) 17 October 1990 (17.10.90), see claims 1, 3. ---	1, 18															
A	EP, A2, 0 305 059 (DOW CORNING) 01 March 1989 (01.03.89), see claim 1. ---	1															
A	EP, A2, 0 350 314 (SHISEIDO) 10 January 1990 (10.01.90), see claims 1, 6. -----	1, 18															
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center;">18 August 1992</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center;">04 SEP 1992</div> </td> </tr> <tr> <td style="width: 50%; padding: 5px;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;">MARCHART e.h.</div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">18 August 1992</div>	Date of Mailing of this International Search Report <div style="text-align: center;">04 SEP 1992</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">MARCHART e.h.</div>											
Date of the Actual Completion of the International Search <div style="text-align: center;">18 August 1992</div>	Date of Mailing of this International Search Report <div style="text-align: center;">04 SEP 1992</div>																
International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">MARCHART e.h.</div>																

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/EP92/01001 SAE 58955

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
in no way liable for these particulars
which are given merely for the purpose
of information.

La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
dans le rapport de recherche inter-
national visée ci-dessus. Les renseigne-
ments fournis sont donnés à titre indica-
tif et n'engagent pas la responsabilité
de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A1	358584	14-03-90	AU A1 41138/89	15-03-90
			BR A 8904492	24-04-90
			FR A1 2636338	16-03-90
			FR B1 2636338	23-11-90
			JP A2 2107639	19-04-90
			US A 5053290	01-10-91
EP A1	392882	17-10-90	AU A1 49700/90	23-08-90
			BR A 9000672	15-01-91
			CA AA 2010161	15-08-90
			FR A1 2642967	17-08-90
			FR B1 2642967	07-06-91
			JP A2 2270816	05-11-90
EP A2	305059	01-03-89	AU A1 20178/88	02-02-89
			AU B2 599504	19-07-90
			EP A3 305059	23-01-91
			GB A0 8718140	09-09-87
			JP A2 2041322	09-02-90
			US A 4992261	12-02-91
			US A 5077422	31-12-91
			US A 4912241	27-03-90
			ZA A 8805830	26-04-89
EP A2	350314	10-01-90	AU A1 37867/89	15-02-90
			AU B2 616538	31-10-91
			EP A3 350314	19-12-90
			KR B1 9109820	30-11-91
			US A 5093511	03-03-92
			JP A2 2117613	02-05-90
			JP A2 2167291	27-06-90